

AUTOXIDATION OF CERTAIN KETONES

by

PHILIP EDWARD MCINTYRE

B. S., Kansas State College  
of Agriculture and Applied Science, 1950

---

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE  
OF AGRICULTURE AND APPLIED SCIENCE

1951

Docu-  
ments  
LD  
2668  
T4  
1951  
M337  
c.2

11

## TABLE OF CONTENTS

INTRODUCTION.....	1
Oxidation Theories.....	1
Structures of Peroxides.....	2
Autoxidation of Ketones.....	5
Statement of Problem.....	6
EXPERIMENTAL.....	7
Equipment.....	7
Oxidation Apparatus.....	7
Distillation Columns.....	10
Infrared Spectrometer.....	11
General Procedures.....	11
Oxidation Runs.....	13
Oxidation of Acetophenone.....	13
Oxidation of Propiophenone.....	14
Oxidation of Isobutyrophenone.....	18
Oxidation of Di-iso-propyl Ketone.....	23
Reaction Rate Studies.....	24
DISCUSSION OF RESULTS AND CONCLUSIONS.....	30
SUMMARY.....	32
ACKNOWLEDGMENT.....	34
LITERATURE CITED.....	35

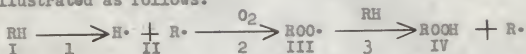
## INTRODUCTION

Interest in the attack by molecular oxygen upon organic compounds has increased greatly during the past several decades. This is evidenced by the voluminous references to this subject in the literature. Examples of the practical applications, both beneficial and detrimental, which perhaps give incentive to this work are such uses as paint and finishes industries, the combustion of motor fuels, the deterioration of rubber and the military uses of explosives and propellants.

### Oxidation Theories

The easily observed phenomena of burning led to many early theories on the oxidation of hydrocarbons such as the preference of burning as advanced by Kersten (20), which had little to substantiate it, followed by the hydroxylation theory of Bone and Wheeler (2,3,4) and the primary dehydrogenation theory of Lewis (22). These early ideas had little basis in fact and as a consequence were rapidly eclipsed by the peroxidation theory. This theory, which is widely held today, was first advanced by Egerton (8) and Egerton and Pidgeon (9). They proposed that the initial product of an oxidation was a reactive peroxy compound which could form a relatively stable peroxide or could undergo decomposition to yield highly activated products. This initial form of Egerton's theory resembled the hydroxylation theory and was greatly extended by the work of Farmer (12) who is largely responsible for the present day concept.

This is basically a free radical type mechanism which may be illustrated as follows:

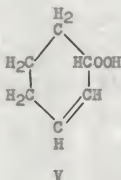


A hydrocarbon molecule (I) was considered to lose a hydrogen atom giving a hydrocarbon free radical (II). Compound (II) could then react with a molecule of oxygen to form a peroxy free radical (III). III could then abstract a hydrogen from another molecule of hydrocarbon to form a hydroperoxide (IV) and the hydrocarbon free radical which is then available to re-enter step 2. The initiation step, the abstraction of the first hydrogen, is not well understood. It is postulated that this step may be initiated by ultraviolet irradiation, thermal energy or by the addition of free radical formers. The formation of the peroxy free radical and the hydroperoxide are chain cycle steps and are the major steps which lead to the formation of peroxides during the oxidation of hydrocarbons. The final reaction products of such oxidations may be complex mixtures of the decomposition products of the hydroperoxides.

### Structures of Peroxides

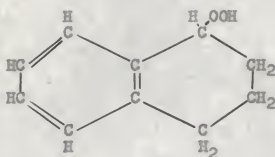
During the early stages of autoxidation studies, only qualitative tests for peroxides were obtained. Subsequently Van der Beek and Jorissen (35) studied the reaction of molecular oxygen with benzaldehyde and isolated perbenzoic acid. This was the first reported peroxidic intermediate ever isolated. In this early period there was much conjecture and speculation about the

structure of peroxides, particularly those formed in olefin type compounds. Such men as Engler and Wild (10), Paquot (28) and Stephens (33) worked with and proposed structures for peroxides. These hypothesized structures were shown to be incorrect when Criegee, Pilz and Flygare (7) oxidized cyclohexene and isolated and identified 3-cyclohexenyl hydroperoxide (V).



This structure was later confirmed by Farmer and Sundralingam (14). Through the extensive work of Farmer and Sundralingam (14), and Farmer and Sutton (15), it was definitely shown that the addition of oxygen can take place without the alteration of a functional group.

The hydroperoxides which are formed during the oxidation of compounds having a saturated group attached or fused to an aromatic ring are similar to that formed with cyclohexene. The alpha-methylenic carbon, in these cases, is that atom adjacent to the unsaturated system. The first such hydroperoxide was isolated from oxidized tetralin by Hock and Susemihl (18) and later studied by Criegee, Pilz and Flygare (7), and was shown to be  $\alpha$ -(ac-tetralyl) hydroperoxide (VI).



VI

These data led naturally to a study of benzene derivatives such as *m*- and *p*-xylene (13, 17), *p*-cymene (15), ethyl benzene and diphenyl methane (17) and others. In each case the hydroperoxide group formed on the carbon atom adjacent to the benzene ring.

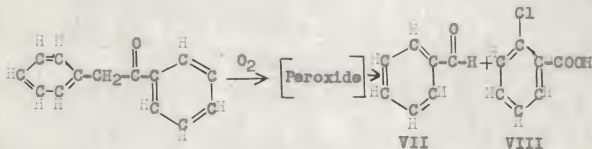
Analysis of the above cited data shows that in every case the hydroperoxide group is attached to a carbon atom which is adjacent to a double bond or unsaturated system. Therefore, the conclusion may be drawn that hydrogen atoms on the alpha carbon positions are apparently more easily removed than hydrogen atoms on other carbons. This fact may be due to the influence of a double bond or aromatic structure. Where two different carbon atoms were adjacent to the double bond, as exemplified by the methyl cyclohexenes, the hydroperoxide group is found on the carbon atom having originally the least number of hydrogen atoms. Thus it is indicated that in a competing reaction the replacement of hydrogen atoms by peroxy groups proceeds in the decreasing order tertiary, secondary, primary.



### Autoxidation of Ketones

There have been very few experiments reported on the oxidation of ketones. One of the first was by Kohler (21) who reported a cyclic peroxidic intermediate in 1907. His conclusions were apparently drawn from the previously cited work on unsaturated hydrocarbons. This proposed cyclic peroxide was shown, many years later, to be incorrect.

Jenkins (19) obtained qualitative tests for peroxides in benzyl *o*-chlorophenyl ketone which had been exposed to the air for a prolonged time. The oxidation products isolated were benzaldehyde (VII) and *o*-chlorobenzoic acid (VIII) which again indicated that the oxygen attacked the  $\alpha$ -methylene position.



Paquot (29) oxidized cyclohexanone, 4-heptanone and 2-octanone in the presence of nickel phthalocyanine but failed to isolate the qualitatively detected peroxides. Paquot's work indicated, by the nature of the products formed, that the oxygen attack was on the secondary carbon adjacent to the carbonyl group. This was substantiated when Rigandy (31), in 1948, through the use of ultraviolet absorption spectra, showed that when 1,1,2,3-tetraphenylpropanone-3 was oxidized the peroxy group was found on

the tertiary carbon atom of 2(1,1,2,3-tetraphenylpropanone-3-yl) hydroperoxide (IX).



This information was further substantiated by Fuson and Jackson (16) and Patton (27).

The results obtained by the aforementioned men indicated that the oxidation of ketones began by the initial attack of an oxygen molecule at the carbon adjacent to the carbonyl group.

#### Statement of Problem

Patton (27) was the only worker of the previously mentioned men who actually started to investigate the autoxidation of ketones. The other workers made their contributions to structure by attempting to identify reaction products. This paper then, is a continuation of Patton's work. The conditions used were as follows: exclusion of inorganic catalysts, rate studies, infrared studies and analysis of final reaction mixtures.

A special all glass reaction apparatus was constructed



(Plate I), in order to follow the kinetics. This apparatus contained a thermostatic temperature control and yet could be adjusted to any desired temperature between  $30^{\circ}$  and  $180^{\circ}$  C. The oxygen gas flow was regulated as to be in excess at all times so that the rate measurements were of the reaction itself.

The method selected for the determination of the rate of reaction consisted of the chemical analysis, at regular intervals, of representative samples drawn from the oxidation apparatus.

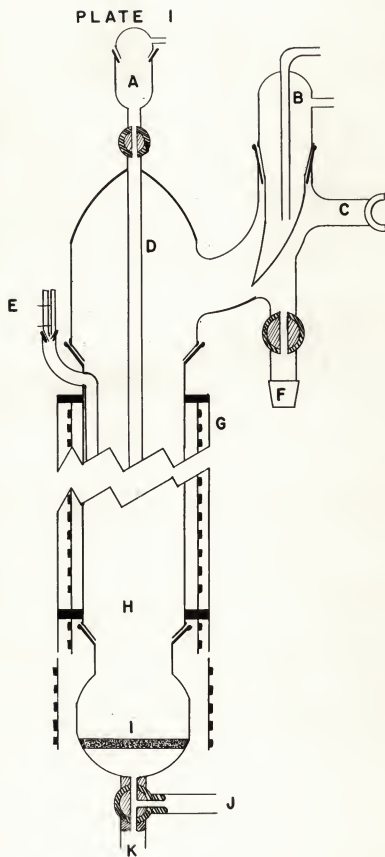
## EXPERIMENTAL

### Equipment

Oxidation Apparatus. The oxidation apparatus (Plate I) consisted of a 25 mm O. D. Pyrex glass tube four feet long to which had been fastened a 29/42 standard taper ground glass inner joint at one end and at the other end a 40/50 standard taper ground glass outer joint. This constituted the reaction chamber. A 29/42 outer joint was affixed to a 30 mm sintered glass buchner type funnel of medium porosity which had been fused to a six mm three way stopcock. This piece formed the bottom of the reaction chamber. The reaction chamber was fixed inside of a slightly larger Pyrex glass tube which had been wound with Chromel resistance ribbon. These two concentric tubes were in turn fixed inside of a third larger Pyrex tube which served as insulation and protection for the inner tubes. The 40/50 ground

# EXPLANATION OF PLATE I

- A. Sample collecting tube.
- B. Water cooled condenser.
- C. Outlet for volatiles and oxygen escape.
- D. Sampling tube.
- E. Mercury contact switch.
- F. Removal of low boiling fractions.
- G. Heating jacket.
- H. Oxidation chamber.
- I. Sintered glass disc.
- J. Oxygen inlet tube.
- K. Drain.



glass joint at the top of the column served as a means of connecting a "Y" shaped head. One arm of the head contained a cold finger type condenser and a side opening fitted with an 18/9 spherical outer joint. The other arm was connected to a piece of nine mm Pyrex tubing which reached into the center of the oxidation chamber. This tube was connected at the top to a receiver with a stopcock which was used as a sampler reservoir. The 18/9 joint was used to connect a dry ice-cooled trap for the collection of volatile products. The temperature of the oxidation mixture was visually observed on a thermometer which had been encapsulated in glass tubing, containing a small amount of mercury, and the capsule suspended by glass cord in the liquid. The operating temperature was regulated within  $\pm 1^{\circ}$  C. by means of a mercury filled glass tube which was sealed to the inside of the oxidation chamber and opened to the outside of the tube by means of a ring seal in the side of the oxidation chamber above the heating and insulation jackets. This mercury filled tube had fused to it a 10/30 standard taper outer joint. The corresponding inner joint had fused, in its side, a piece of tungsten wire close to the ground glass area. The heat input was regulated by means of a series of relays and a variable transformer.

Distillation Columns. Two distilling columns were used throughout this research problem for the purification and separation of reactants and products. Both columns were of the adiabatic type so constructed as to use an interchangeable

total condensation, variable take-off stillhead. One column was of 20 mm O. D. Pyrex glass tubing, 48 inches in length, and packed with three eighths inch Pyrex glass helices. The second column was of 25 mm O. D. Pyrex glass, 28 inches in length, and was also packed with the same type of helices. Both columns were equipped to operate at either atmospheric or reduced pressure. The reduced pressures were obtained with a Welch Duo-Seal two stage vacuum pump which was connected in parallel with a Cenco Hi-Vac vacuum pump. Pressures were measured with a tipping McLeod gauge.

Infrared Spectrometer. The infrared spectrometer was a Perkin-Elmer Model 12C Recording Spectrometer which could be used with either a lithium fluoride or sodium chloride prism. The sample cells were optically flat sodium chloride plates separated by aluminum foil spacers and fitted with a hypodermic needle for filling purposes. The cells were filled by means of a glass syringe and flushed out in the same manner after using.

#### General Procedures

The mechanical procedure as outlined here was followed for all oxidations.

Prior to each experiment, the oxidation chamber was cleaned, and the oxidation performed, as outlined by Patton (27), with the exception that the column was heated to approximately 70° C. during the final drying operation.

The peroxide formation was followed by a slight modification

of the method of Wagner, Smith and Peters (36). A weighed sample of the peroxide containing mixture was added to 40 ml of iso-propyl alcohol (Baker and Adamson, 1196) in a 250 ml iodine flask fitted with a ground glass condenser. Carbon dioxide (Pure Carbonic Products Corp.) was passed into the flask for three minutes by means of a glass tube inserted through the condenser. Glacial acetic acid (Du Pont, reagent grade), two ml, and ten ml of a saturated solution of sodium iodide (Baker and Adamson, 2260) in iso-propyl alcohol were added. The mixture was refluxed for 15 minutes, carbon dioxide again was passed into the flask, and the liberated iodine was titrated with a standard solution of sodium thiosulfate.

The acid content of samples was determined by direct titration with standard alkali of a weighed sample of reaction mixture in 20 ml of iso-propyl alcohol.

The samples used in each of the determinations were weighed in one of two ways. Initially the weight was obtained by removing a small quantity of the reaction mixture from a weighed 25 ml Erlenmeyer flask fitted with a tightly fitting stopper, which had a medicine dropper inserted through it, then reweighing the flask and obtaining the weight of the mixture removed by difference. This method led to a fairly large error due to loss of volatile components of a three component system. This evaporation error was reduced by placing the samples directly into tared weighing bottles. The sample, bottle and stopper, were placed in the Erlenmeyer flask and analyzed as before.



Infrared spectra of the samples were obtained with the Perkin-Elmer spectrometer by Dr. Stuart E. Whitecomb and assistants of the Department of Physics.

#### Oxidation Runs

Oxidation of Acetophenone. Approximately one liter of acetophenone (Matheson 2221 and/or Eastman 496) was fractionated through the 48 inch column at a pressure of 5 mm and a reflux ratio of eleven to one. The distillate was discarded until the head temperature remained constant for the distillation of 25 ml. The temperature remained constant over a one degree range. The distillate had a m. p. of  $20.1^{\circ}\text{C.}$ ,  $n_D^{20}$ , 1.5361 and  $d_4^{20}$ , 1.038. The literature values for these constants were: m. p.,  $20.5^{\circ}\text{C.}$  (5),  $n_D^{20}$ , 1.5342 (5), and  $d_{15}^{15}$ , 1.0329 (11).

Three oxidations runs were made under the following conditions:

<u>Temperature</u>	<u>Sampling intervals</u>	<u>Length of oxidation</u>
130° C.	1½ hours	20.5 hours
130° C.	½ hours	5 hours
160° C.	8 hours	87 hours

A slight discoloration was observed in all cases, however there was no peroxide formation and only a very slight acid increase. Distillation of the contents of the column, after treatment with oxygen, gave, in every case, a dark brown semisolid pot residue which was slightly acidic in character, but attempts to further identify it were unsuccessful.

A fourth run was made at a temperature of  $160^{\circ}$ - $170^{\circ}$  C. with dry nitrogen gas being used instead of oxygen for a period of 168 hours. The same discoloration was observed as with oxygen, however, the rate of formation seemed to be slower. Distillation of this reaction mixture also yielded the same type of residue as that obtained previously.

Oxidation of Propiophenone. Propiophenone (ethyl phenyl ketone, Eastman 1235) was fractionated through the 43 inch column at a pressure of 5 mm. The constant boiling fraction which was used in all oxidations had the following physical constants:  $d_4^{20}$ , 1.011 and  $n_D^{20}$ , 1.5272. The following values were recorded in the literature for these constants:  $d_{20}^{20}$ , 1.012 (37) and  $n_D^{20}$ , 1.5270 (37).

The oxidation apparatus was filled with 514 grams of propiophenone and the temperature raised to  $130^{\circ}$  C. Oxygen was passed through the ketone for 50.5 hours. Samples were withdrawn at three hour intervals for 15 hours, then at 27.5 and 50.5 hours. The acid and peroxide content were determined on each sample and the infrared absorption spectrum was also obtained for each sample. Oxidations were also run at  $160^{\circ}$  C. for 29.5 hours and  $140^{\circ}$  C. for ten hours. The results of the  $130^{\circ}$  C. and  $140^{\circ}$  C. oxidations are shown by the curves in Figs. 1 and 2.

The final oxidation mixture from the column was examined separately from the material collected in the dry ice-cooled trap. The mixture drained from the oxidation apparatus was

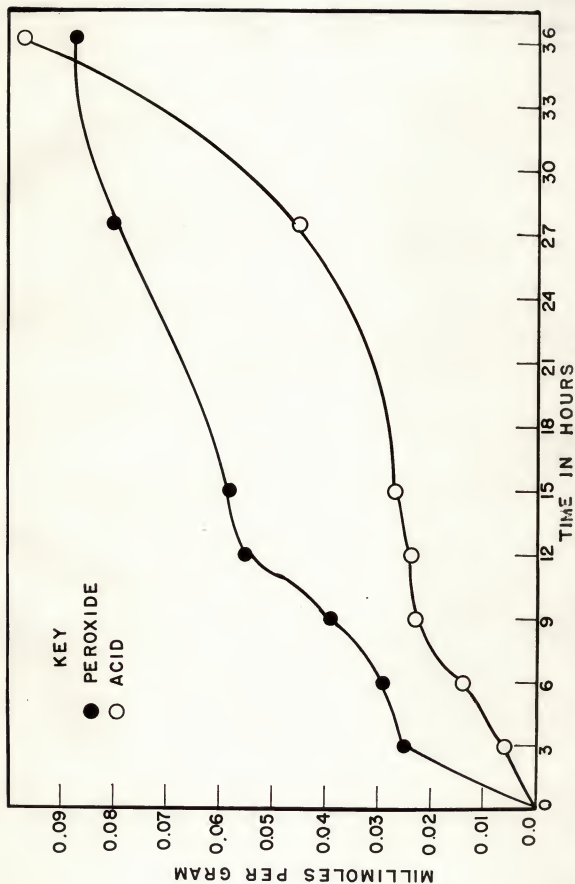


FIG.1 OXIDATION OF PROPIOPHENONE 130° C.

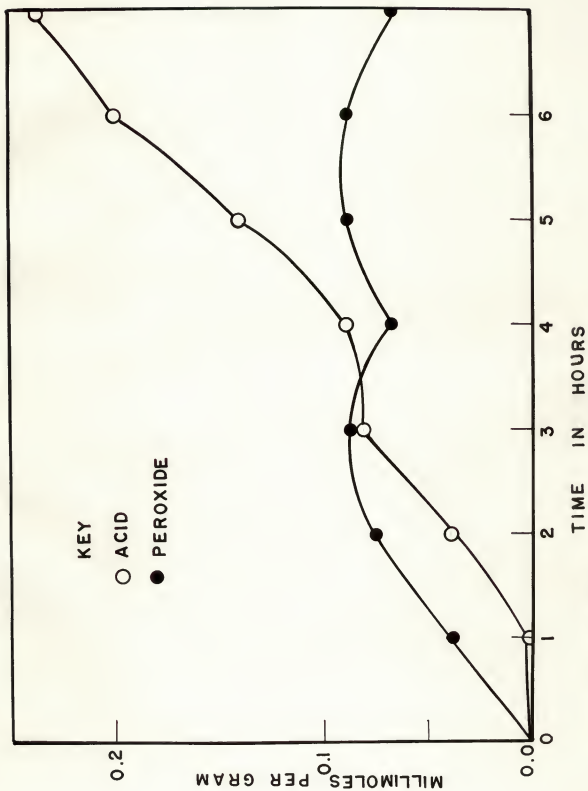


FIG. 2 OXIDATION OF PROPIOPHENONE 140° C.

washed with several 100 ml portions of ten percent sodium hydroxide until the organic liquid was neutral to phenolphthalein. The aqueous alkaline solution was washed twice with 100 ml portions of ether and the ether recombined with the original organic material. The aqueous solution was placed in a four liter Erlenmeyer flask and carbon dioxide gas passed through the liquid for 24 hours. This basic solution was washed with three 50 ml portions of ether. Distillation of the ether extracts resulted in the isolation of a small amount of a tarry semisolid. This solid was a dark reddish brown color and was acidic in nature. It gave a positive ferric chloride test but defied all further attempts to identify it.

The alkaline solution was neutralized with hydrochloric acid and a white fluffy solid was removed by filtration. This acid was recrystallized from hot water and had a corrected m. p. of  $120^{\circ}$ - $121^{\circ}$  C., a neutral equivalent of 122, 124 and 126. The anilide prepared from this acid had a m. p. of  $158^{\circ}$ - $159^{\circ}$  C. The literature values for benzoic acid are: m. p.,  $121^{\circ}$  C. (26); neutral equivalent, 122 (26), and benzanilide m. p.,  $160^{\circ}$  C. (26).

The neutral organic liquid was placed in a 500 ml round bottomed two-neck flask equipped with a capillary ebulliator and a Claisen type head and water cooled fraction cutter. The pressure in the system was lowered to 3.5 mm and the liquid was distilled. All but 8.8 grams of the liquid distilled at a constant temperature and was shown to be propiophenone. No qual-

itative test for a peroxide could be obtained with either the distillate or the pot residue. The residue was of the same general nature as that described previously for acetophenone.

The liquid obtained from the dry ice-cooled trap was placed in a 50 ml flask fitted with a ground glass "L" shaped tube which was in turn connected to a small dry ice-cooled trap. The 50 ml flask was heated only to room temperature and allowed to stand for 24 hours. At the end of that period of time a clear colorless liquid had collected in the ice trap. The 2,4-dinitrophenylhydrazone prepared from this liquid had a m. p. of  $166^{\circ}$ - $167^{\circ}$  C. and semicarbazone had a m. p. of  $165^{\circ}$ - $167^{\circ}$  C. The literature values for acetaldehyde derivatives are  $168^{\circ}$  C. (26) and  $169^{\circ}$  C. (26) for the 2,4-dinitrophenylhydrazone and semicarbazone, respectively. Further distillation of the pot residue yielded only a small quantity of propiophenone.

Attempts made to isolate and identify the hydroperoxide intermediate were always unsuccessful as the peroxide decomposed when concentrations of approximately 0.2 millimoles per gram was reached.

Oxidation of Isobutyrophenone. The isobutyrophenone (isopropyl phenyl ketone) used in these oxidations was prepared by a Friedel-Crafts synthesis using the proportions established by Schmidt (32). The crude ketone was fractionated through the 48 inch column at a pressure of eight mm of mercury. The constant boiling fraction had the following physical constants:  $n_D^{20}$ , 1.5190,  $d_4^{20}$ , 0.990. A 2,4-dinitrophenylhydrazone had a corrected m. p. of  $160^{\circ}$ - $161^{\circ}$  C. Literature values for the above were



$n_D^{16.6}$ , 1.5192 (1);  $d_4^{16.6}$ , 0.987 (1) and the derivative m. p. 163° C. (26).

Two scouting runs were made at temperatures of 120° C. and 140° C., Fig. 3, and it was observed that the reaction rate was quite slow. A third oxidation was conducted at a temperature of 150° C., Fig. 4, using 584 grams of isobutyrophenone. The reaction stopped itself due to the formation of benzoic acid which solidified in the oxygen inlet tube sometime between 10.5 and 23.5 hours. The reaction mixture drained from the column was separated in the same manner as that of propiophenone, yielding benzoic acid, unreacted ketone and some dark brown tarry residue. The dry ice-cooled trap contained 49.8 grams of a colorless liquid. The liquid gave a positive test to Fehling's solution indicating the presence of a reducing group. The liquid was placed in a 100 ml round bottomed flask equipped with a ten inch Vigreux column attached to a small dry ice-cooled trap, the pot temperature was held at 30° C. for two hours, the distillate weighed less than 0.8 gram and gave a strong Fehling's test and Tollens' test. A 2,4-dinitrophenylhydrazone had a m. p. of 165°-167° C. The literature value for the corresponding derivative of acetaldehyde is 169° C. (26). A mixed m. p. with the derivative of authentic acetaldehyde showed no depression. A second fraction weighing 43 grams was collected at a boiling range of 54°-57° C. This fraction formed a semicarbazone having a m. p. of 183°-184° C. and a 2,4-dinitrophenylhydrazone m. p., 124°-125.5° C. Literature values for the corresponding derivatives

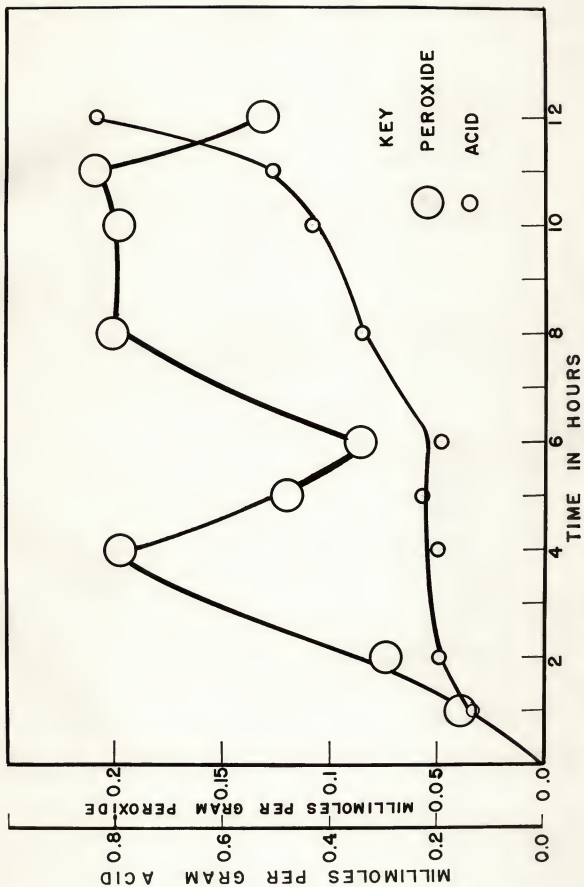


FIG.3 OXIDATION OF ISOBUTYROPHENONE, 140° C.

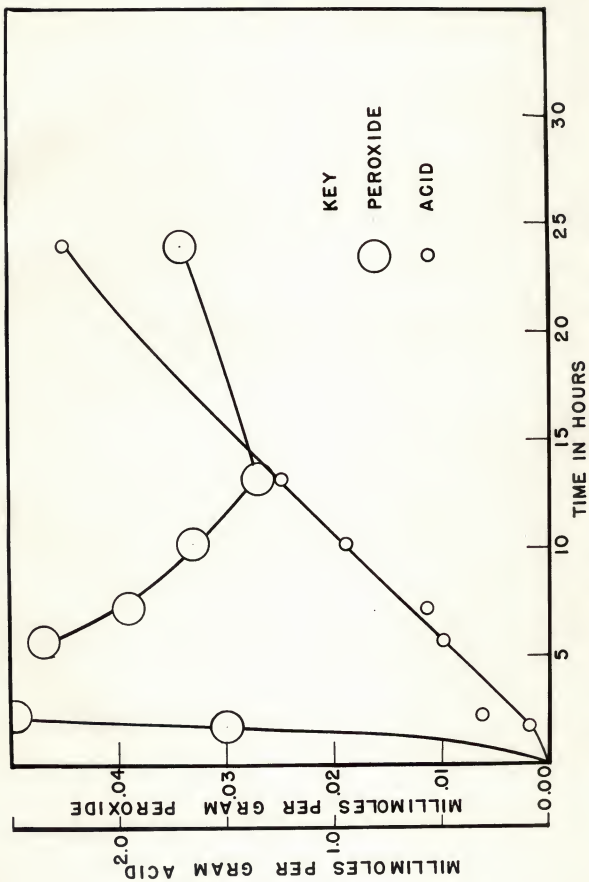


FIG.4 OXIDATION OF ISOBUTYROPHENONE 160°C.

of acetone are  $190^{\circ}$  C. (26) and  $128^{\circ}$  C. (26) respectively. Mixed melting points with derivatives from authentic acetone showed no depression. The third fraction weighed 1.2 grams and was collected from  $90^{\circ}$  to  $112^{\circ}$  C. It was acidic to litmus and water soluble. It gave the following Du Claux values: 7.0, 7.0, 7.2. Its anilide and p-bromophenacyl ester had melting points of  $111^{\circ}$ - $112^{\circ}$  C. and  $82^{\circ}$ - $84^{\circ}$  C., respectively. The above listed properties of acetic acid are, Du Claux values, 6.8, 7.1, 7.4 (26); acetanilide m. p.,  $114^{\circ}$  C. (26), and p-bromophenacyl acetate m. p.,  $85^{\circ}$  C. (26). The pot residue proved to be isobutyrophenone (1.6 grams).

The acid free organic liquid from the oxidation column was divided into two equal quantities and attempts were made to isolate the peroxide intermediate. One portion was placed in a 500 ml round bottomed flask equipped with a capillary ebulliator and attached to a Claisen type distilling head which was in turn connected to a water cooled fraction cutter. The pressure in the system was reduced to 0.1 mm of mercury and the temperature slowly raised. At a head temperature of  $103^{\circ}$ - $107^{\circ}$  C. the ketone distilled quite readily. When the ketone stopped distilling, the Glascol mantle temperature was increased and there was a rapid increase in the temperature to  $127^{\circ}$  C. A slight explosion occurred which blew the thermometer from the distilling head. Analysis of the pot residue showed only trace amounts of peroxide remaining.

The second portion of the neutral oxidation products was

passed rapidly through a steam heated flash evaporator (6), several times. The peroxide enriched portion contained approximately 0.35 millimoles per gram of peroxide. After this concentration was reached the ketone apparently co-distilled for the peroxide content of both the residue and distillate remained constant.

Oxidation of Di-iso-propyl Ketone. Di-iso-propyl ketone (Eastman P3244) was fractionated through the 48 inch column under dry nitrogen. The constant boiling fraction was collected at a temperature of  $111^{\circ}\text{C}$ . at a pressure of 732.8 mm. The collected fraction had the following physical properties;  $d_4^{20}$ , 0.800 and  $n_D^{20}$ , 1.4012. The following values were recorded in the literature for these constants; b. p.,  $123.7^{\circ}\text{C}$ . at 760 mm (30);  $d_4^{20}$ , 0.806 (30);  $n_D^{20}$ , 1.4007 (34).

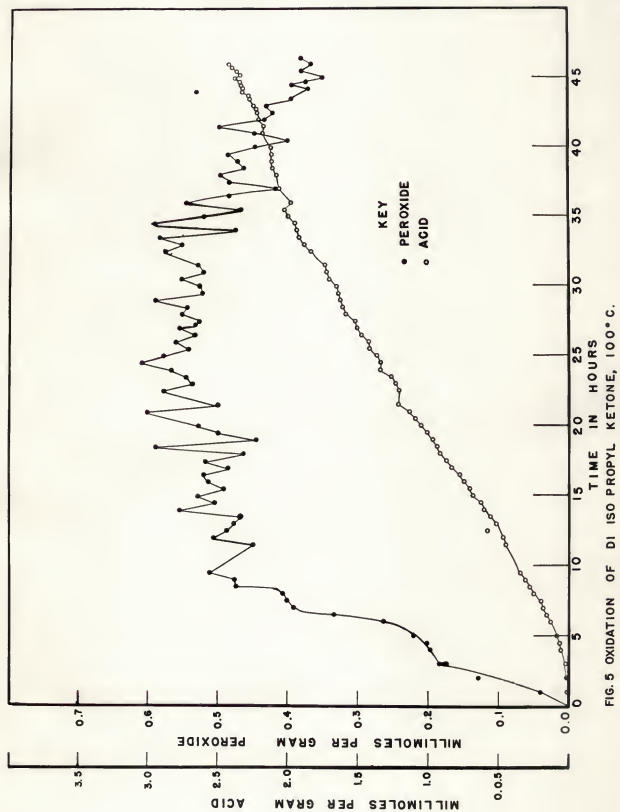
Four oxidations of di-iso-propyl ketone were performed for the purpose of studying the kinetics of the reaction. The procedure used in each of the following cases differed from the previous oxidations. Firstly, dry nitrogen gas was passed through the liquid in the apparatus during the time that it was being brought to the operating temperature. Secondly, no attempt was made to isolate and identify the oxidation products remaining in the column after the oxidation had been discontinued. The dry ice-cooled trap was used only once, the contents were analyzed and were shown to be largely the same as reported by Patton (27). In addition, there was detected a small amount of water and carbon dioxide. The presence of water was proven by shaking a

small quantity of the trap liquid with anhydrous cupric sulfate and observing the development of a blue color and further substantiated by adding a few drops of the liquid to metallic sodium and collecting and burning the evolved gas. The presence of carbon dioxide was shown by placing the trap liquid in a flask which had been fitted with a tight rubber stopper. Through this stopper a piece of bent glass tubing had been inserted and the other end of the glass tubing opened under the surface of a test tube containing a solution of barium hydroxide. As the trap residue warmed to room temperature a dense white precipitate of barium carbonate formed in the test tube. The results of the chemical analysis of the oxidation of di-iso-propyl ketone at temperatures of  $100^{\circ}\text{C}$ . and  $110^{\circ}\text{C}$ . are shown on Figs. 5 and 6. Infrared curves in the 2.960 and 3.079 micron regions which qualitatively represent the peroxide and acid respectively, are shown on Figs. 7 and 8.

#### Reaction Rate Studies

Analyses of the oxidation curves shown in Figs. 5 and 6 indicate that the oxidation rate is not a simple first order reaction as has been previously reported (27). A periodicity seems to be indicated, since qualitatively it can be observed that in most cases where a decrease appears in the peroxide concentration, the rate of change of acid concentration shows an increase. Correspondingly, at the times where the rate of peroxide formation is increasing, the rate of formation of acid is slower than in the former case. The qualitatively indicated





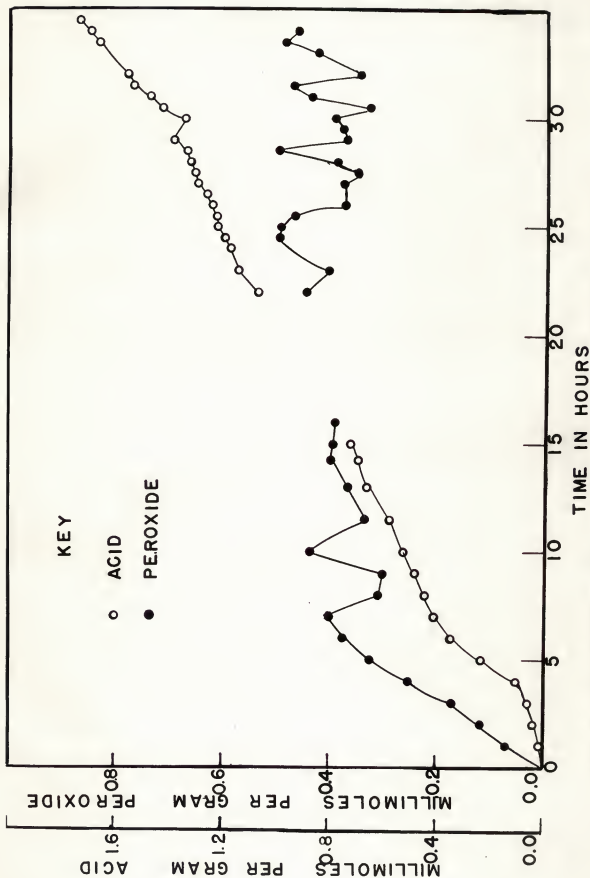


FIG. 6 OXIDATION OF DI-ISOPROPYL KETONE 110 °C.

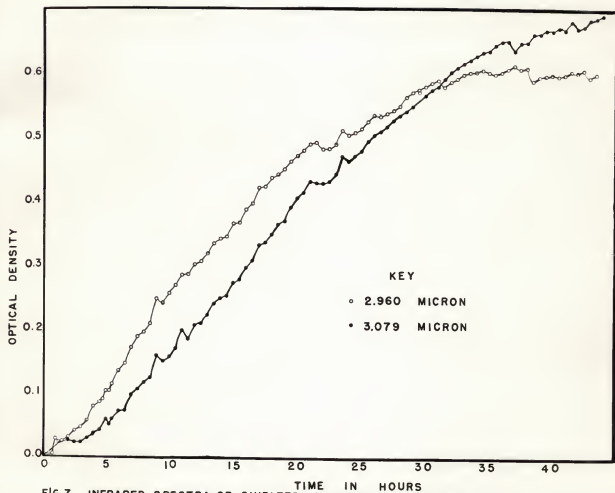


FIG.7 INFRARED SPECTRA OF OXIDIZED DI-ISO-PROPYL KETONE- 100° C.

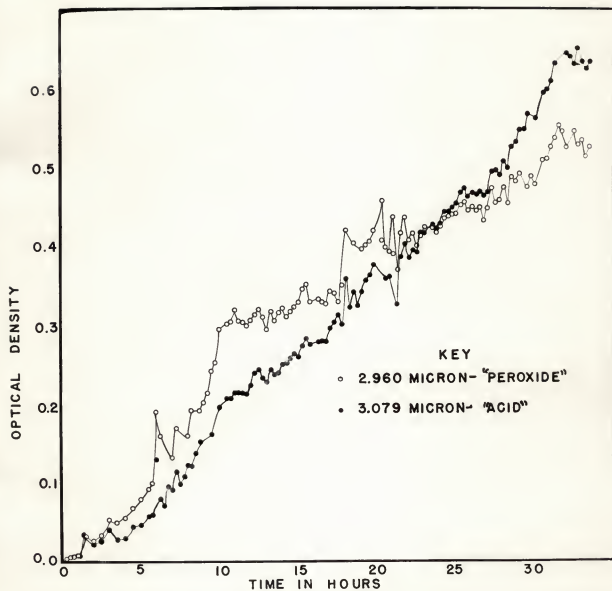
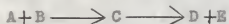
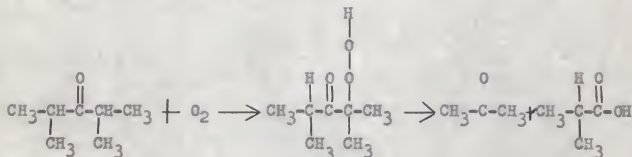


FIG. 8 INFRARED SPECTRA OF OXIDIZED DI-ISO-PROPYL KETONE, 110°C.

periodicity may have a magnitude of plus or minus ten percent deviation from a mean value of peroxide concentration. The peroxide determination, as reported by Wagner, Smith and Peters (36), has a stated accuracy of two percent, which has been confirmed experimentally in this laboratory. Lotka (25) reported that this type of curve is characteristic of a reaction which proceeds by two consecutive first order steps which are concomitantly autocatalytic. The suggested course of the reaction could be shown in the following sequences:



The illustration as applied to the autoxidation of di-iso-propyl ketone then would be as shown below.



If the concentration of ketone and oxygen is constant and the peroxide autocatalyzes its own formation and also the acid autocatalyzes its own formation, then this particular case might well be a periodic reaction of the type reported by Lotka. The concentration of the ketone is in large excess during the first portion of the reaction and also the concentration of oxygen would be held constant due to its limited solubility. These two conditions satisfy the requirements of the initial reactants in the Lotka treatment of similar data.

The infrared data shown in Figs. 7 and 8 also seem to

indicate a periodicity. These infrared data are semi-quantitative in nature and consequently they do not show the calculated curves for acid and peroxide formation separately. In the wavelength regions indicated in Figs. 7 and 8 there is a slight overlapping of the -OH group of the hydroperoxide and the -OH group of a carboxylic acid. These calculations and this resolution of the infrared curve into its acidic and peroxidic components will be covered by Mr. W. A. Porter in his master's thesis.

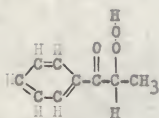
The study of the rate of this oxidation is being examined in detail at present and pending further results, no definite statement regarding the kinetics of oxidation can be made. Due to time limitations, this work cannot be included in this thesis.

#### DISCUSSION OF RESULTS AND CONCLUSIONS

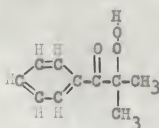
Analysis of the data presented indicates that in all cases, except that of acetophenone, a peroxide was formed before detectable amounts of acid appeared. In view of the fact that a peroxide had been isolated previously (27) from oxidized di-isopropyl ketone and appeared to be the precursor of the final products, it seemed probable that a peroxide was the first thermodynamically stable compound formed by each of the ketones which underwent a change when subjected to molecular oxygen.

Considering the data of Patton (27) and Rigaudy (31), the following structures are suggested for the hydroperoxides of propiophenone (VII), and isobutyrophenone (VIII).





VII



VIII

Acetophenone apparently does not undergo oxidation, at least, at the conditions used in this research. The formation of color and small amount of acidic material are due to pyrolysis as shown qualitatively by the treatment of the ketone with dry nitrogen at an elevated temperature.

The reaction curves for propiophenone and isobutyrophenone, Figs. 1,2,3 and 4, do not appear to be consistent or regular in the increase of peroxide, therefore, the conclusion can be drawn that the initial formation of peroxide is quite rapid as compared to the formation of the acid and by analogy to the reaction curves of di-iso-propyl ketone it can be assumed that the irregularity of the points on the peroxide line may be due to a periodic curve of the type shown by Figs. 5 and 6.

The kinetics study of di-iso-propyl ketone indicates the possibility of a periodic reaction. A general reaction of the type A plus B yielding C which in turn decomposes to give D and E has been illustrated by Patton (27). He oxidized di-iso-propyl ketone and succeeded in isolating the products formed. Patton found, in addition to hydroperoxide, almost equimolar quantities of acetone and isobutyric acid. These data fit the general formula given above. Further, he proved that upon de-

composition, the peroxidic compound gave only acetone and isobutyric acid. If the concentration of ketone and oxygen are constant and the peroxide and acid are concomitantly autocatalytic, then this particular case might well be a periodic reaction of the type reported by Lotka.

While the data described in this thesis do not agree with the rates of reaction obtained by Patton (27), it does tend to substantiate his assumption that the rates he calculated were specific for the apparatus used.

#### SUMMARY

Preliminary studies on the effect of molecular oxygen on a series of alkyl aryl ketones have shown that oxidation takes place with those ketones having a secondary or tertiary carbon atom adjacent to the carbonyl group. Ketones having a primary carbon atom adjacent to the carbonyl group apparently are unaffected by molecular oxygen, but do undergo a small amount of pyrolysis at the elevated temperature used.

Qualitative tests indicated that a peroxide was an intermediate in both of the cases where oxidation took place. The hydroperoxides of the ketones apparently decomposed to yield either an aldehyde or a ketone and, in the case of isobutyrophenone, both an aldehyde in trace quantities and a ketone were proven. In addition to the aldehyde and/or ketone an aryl fragment was also formed which was converted eventually to the corresponding acid.

It was not possible to determine definitely the kinetics

involved in these ketone oxidations. Data obtained on the oxidation of di-iso-propyl ketone tend to show that the reaction is not of a simple nature but is indicative of two consecutive reactions, each of which autocatalyzes the other. A great deal more work will be necessary before a positive statement can be made on this subject.

The work on this project did not lead to the isolation of any new hydroperoxides, however the qualitative proof of the peroxidic intermediates formed seems to lend proof to the peroxidation theory as most adequately explaining the course of reaction of propiophenone and isobutyrophenone.

## ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Dexter B. Sharp, for his many helpful suggestions and long days and nights of unselfish assistance on this problem. The author would also like to acknowledge the assistance of Dr. Stewart E. Whitcomb and his assistants, A. Dwight Moorhead and William A. Porter, of the Kansas State College Department of Physics for their many hours of tedious work on the infrared spectra and for their invaluable assistance on the temperature regulator system used on the oxidation apparatus. Thirdly, the author wishes to thank Dr. M. K. Testerman of the Kansas State College Department of Chemistry for his help in analyzing the kinetics involved and his physical assistance on the laborious analytical work. Finally, the author wishes to express his appreciation to the Office of Naval Research, whose financial assistance made this research possible.

## LITERATURE CITED

1. Auwers, Eisenlohr.  
Jour. f. Prakt. Chem. 82:132. 1936. Original not seen. Data given in Beilstein's Handbuch fur Organischen Chemie. Band 7. p. 316.
2. Bone, William A., and R. V. Wheeler.  
The slow oxidation of methane at low temperatures. (London) Chem. Soc. Jour. 81:535-548. 1902.
3. Bone, William A., and R. V. Wheeler.  
The slow oxidation of methane at low temperatures. Part II. (London) Chem. Soc. Jour. 83:1074-1087. 1903.
4. Bone, William A., and R. V. Wheeler.  
The slow oxidation of ethylene. (London) Chem. Soc. Jour. 85:1637-1661. 1904.
5. Bruhl.  
Jour. f. Prakt. Chem. Part 2, 50:311. 1899. Original not seen. Data given in Beilstein's Handbuch fur Organischen Chemie. Band 7. p. 272.
6. Ciereszko, Leon S.  
A simple laboratory vacuum flash evaporator. Abstract of papers, Fifth Southwest Regional Meeting, Amer. Chem. Soc., Oklahoma City, Okla. Dec. 8-10, 1949. p. 23.
7. Criegee, Rudolf, H. Pilz, and H. Flygare.  
Zur kenntnis der olefin peroxyde. Deut. Chem. Gesell. Ber. 72:1799:1804. 1939.
8. Egerton, A.  
The combustion of hydrocarbons. Peroxidation theory. Nature. 121:10. 1928. Original not seen. Abstract in Chem. Abs. 22:4236. 1928.
9. Egerton, A., and L. M. Pidgeon.  
Absorption spectra of burning hydrocarbons, Roy. Soc. London. Proc., Ser. A. 142:26-39. 1933.
10. Engler, C., and W. Wild.  
Uber die sogenannte "aktivierung" des Saurstoffe und uber superoxydbildung. Deut. Chem. Gessell. Ber. 30:1669-1728. 1897.

11. Eijkman.  
Chemisches Zentralblatt. I:1259. 1904. Original  
not seen. Data given in Beilstein's Handbuch für  
Organischen Chemie. Band 7. p. 272.
12. Farmer, Ernest H.  
 $\alpha$ -methylenic reactivity in olefinic and polyolefinic  
systems. Faraday Soc. Trans. 38:340-348. 1942.
13. Farmer, Ernest H., and G. Narracott.  
Autoxidizability of alkyl groups in xylene. (London)  
Chem. Soc. Jour. 1942:1851-1858. 1942.
14. Farmer, Ernest H., and A. Sundralingam.  
Autoxidation studies in polyisoprene and allied com-  
pounds. I. Structure and reactive tendencies of  
simple olefins. (London) Chem. Soc. Jour. 1942:121-  
142. 1942.
15. Farmer, Ernest H., and D. A. Sutton.  
The course of autoxidation reactions of polyisoprene  
and allied compounds. Part XI. Double bond movement  
during the autoxidation of a mono-olefin. (London)  
Chem. Soc. Jour. 1946:10-13. 1946.
16. Fuson, R. C., and H. L. Jackson.  
Conjugate addition of mesitylmagnesium bromide to  
ethyl 2,4,6-trimethylcinnamate and to mesitalaceto-  
mesitylene. Amer. Chem. Soc. Jour. 72:1637. 1950.
17. Hock, Heinrich, and S. Lang.  
Autoxydation von kohlenwasserstoffen. VII. Über  
peroxyde einfachen benzolkohlenwasserstoffen. Deut.  
Chem. Gesell. Ber. 76B:169-172. 1943.
18. Hock, Heinrich, and W. Susemihl.  
Autoxydation von kohlenwasserstoffen. Über ein durch  
autoxydation erhaltenes tetrahydro-naphthalin-peroxyde.  
Deut. Chem. Gesell. Ber. 66:61-68. 1933.
19. Jenkins, Sanford S.  
The auto-oxidation of ketones. Amer. Chem. Soc. Jour.  
57:2733. 1935.
20. Kersten, O.  
Jour. f. Prakt. Chem. 84:311. 1861.
21. Kohler, E. P.  
The reaction between unsaturated compounds and organic  
magnesium compounds. Amer. Chem. Soc. Jour. 36:185.  
1906.



22. Lewis, John S.  
Low temperature oxidation of hydrocarbons. (London)  
Chem. Soc. Jour. 129:1555-72. 1927.
23. Lewis, John S.  
Low temperature oxidation of hydrocarbons. Part I.  
The pressure-temperature curves for amylene-oxygen  
mixtures. (London) Chem. Soc. Jour. 131:759-767.  
1929.
24. Lewis, John S.  
Low temperature oxidation of hydrocarbons. Part II.  
The ignition of some hydrocarbons in oxygen. (London)  
Chem. Soc. Jour. 132:58-74. 1930.
25. Lotka, A. J.  
Undamped oscillations derived from the law of mass  
action. Amer. Chem. Soc. Jour. 42:1595. 1920.
26. McElvain, S. M.  
The characterization of organic compounds. New York:  
The Macmillan Company, 1949.
27. Patton, Leo W.  
A study of the autoxidation of ketones. Ph. D. Thesis,  
Kansas State College. August, 1950.
28. Paquot, Charles.  
Autoxidations of ethylene hydrocarbons. Soc. Chim. de  
France, Bul. Doc. 12:120-124. 1945. Original not seen.  
Abstract in Chem. Abs. 40:829. 1946.
29. Paquot, Charles.  
Sur la cinetique d'oxydation des cetonnes. Soc. Chim.  
de France, Bul. Doc. 12:450-452. 1945.
30. Poletaeff, Gregorius.  
Bestimmung der constante der seidetemperature. Deut.  
Chem. Gesell. Ber. 24:1308-1309. 1891.
31. Rigaudy, J.  
Constitution des peroxydes des kohler. (Paris) Acad.  
des Sci. Compt. Rend. 226:1993. 1948.
32. Schmidt, C.  
Einwirkung von phtalimidkalium auf einige sauerstoff-  
haltige halogenverbindungen. Deut. Chem. Gesell. Ber.  
22:3250. 1889.

33. Stephens, H. N.  
Studies in autoxidation. Part I. Cyclohexene peroxide. Amer. Chem. Soc. Jour. 50:568-571. 1928.
34. Terentjew.  
Soc. Chim. de France, Bul. Mem. 4, 37:1557. 1925.  
Original not seen. Data given in Beilstein's Handbuch für Organischen Chemie. Band 1. p. 703. Second supplement.
35. Van der Beek, P. A. A., and W. P. Jorissen.  
Autoxidation of benzaldehyde and the activation of oxygen by this substance. Rec. des Trav. Chim. des Pays-Bas. 45:245-247. 1926. Original not seen.  
Abstract in Chem. Abs. 20:2322. 1926.
36. Wagner, C. D., R. N. Smith, and E. D. Peters.  
Determination of organic peroxides. Analyt. Chem. 19:976. 1947.
37. Wallach, O.  
Zur kenntniss der terpene und der atherischen oele. Justus Leibigs Ann. der Chem. 332:317. 1904.

AUTOXIDATION OF CERTAIN KETONES

by

PHILIP EDWARD McINTYRE

ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE

OF AGRICULTURE AND APPLIED SCIENCE

1951

7461-50-1  
32-3-17-3  
9-11-19-17

Preliminary studies of the effect of molecular oxygen on a series of three alkyl aryl ketones, namely, acetophenone, propiophenone and isobutyrophenone have shown that oxidation takes place with those ketones having a secondary or tertiary carbon atom adjacent to the carbonyl group. Those ketones having a primary carbon atom adjacent to the carbonyl group apparently are unaffected by molecular oxygen under the conditions used in this research, but do undergo a small amount of pyrolysis at an elevated temperature.

Qualitative tests indicated that a peroxide was an intermediate product in each of the cases where oxidation took place, although a pure hydroperoxide was not isolated from either of these reactions. The hydroperoxides of the ketones apparently decomposed to yield either an aldehyde or a ketone. In the case of isobutyrophenone, both acetaldehyde in trace amounts and acetone were products of the oxidation. In addition to the aldehyde and/or ketone, an aryl fragment was formed which was converted eventually to the corresponding acid.

In order to study in detail the kinetics involved in these reactions, di-iso-propyl ketone was oxidized at temperatures of 100° C. and 110° C. Data obtained on the oxidation of this ketone tend to show that the reaction is not of a simple nature but involves at least two consecutive reactions, each of which autocatalyzes the other. This type of reaction is indicated by a plot of the concentrations of products as a function of the oxidation time. This graph is periodic in nature, which is characteristic of two consecutive autocatalytic first order

reactions. While the frequency was not definitely established, the peroxide formation curve, and to a lesser degree, the acid formation curve, indicated a real periodic nature.

The work on this project did not lead to the isolation of any new peroxides. However, qualitative evidence of a peroxidic intermediate suggests that the oxidations of propiophenone and isobutyrophenone are best explained by the peroxidation theory as developed by Farmer.